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(56) Documents Cited

EP 0788829 A1 **EP 0682975 A1**
EP 0577438 A2
WPI Abstract AN 2000-621293 [60] & JP 2000213334 A
WPI Abstract AN 1998-550096 [46] & JP 010244155 A
WPI Abstract AN 1995-260189 [45] & JP 070163878 A
WPI Abstract AN 1995-370618 [48] & JP 070251072 A

(58) Field of Search

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(54) Abstract Title

Removal of nitrogen oxides from effluent gases

(57) The selective catalytic reduction of nitrogen oxides (NO_x) over a silver alumina catalyst is improved by using a controlled mixture of hydrocarbon reductant. A preferred constituent of the reductant mixture is formaldehyde. The reduction activity of the silver alumina catalyst, reducing NO_x to N₂, is improved over the typical temperature range of vehicle exhaust gases, and especially at lower temperatures.

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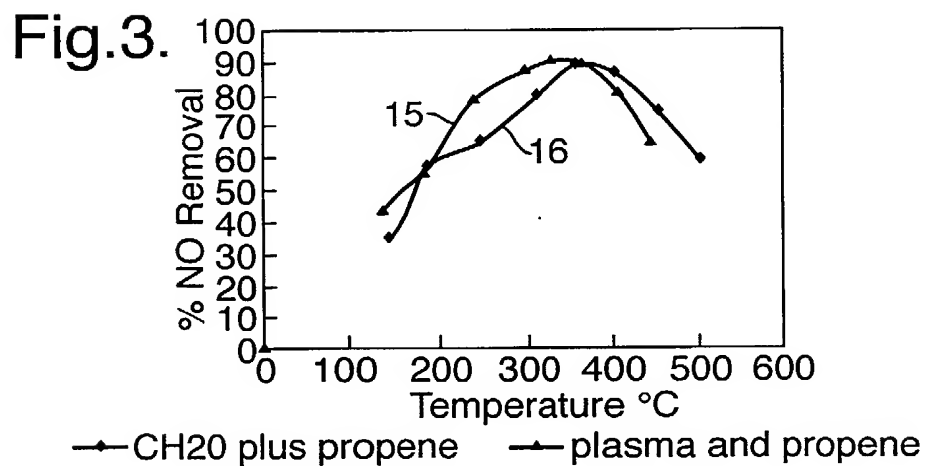
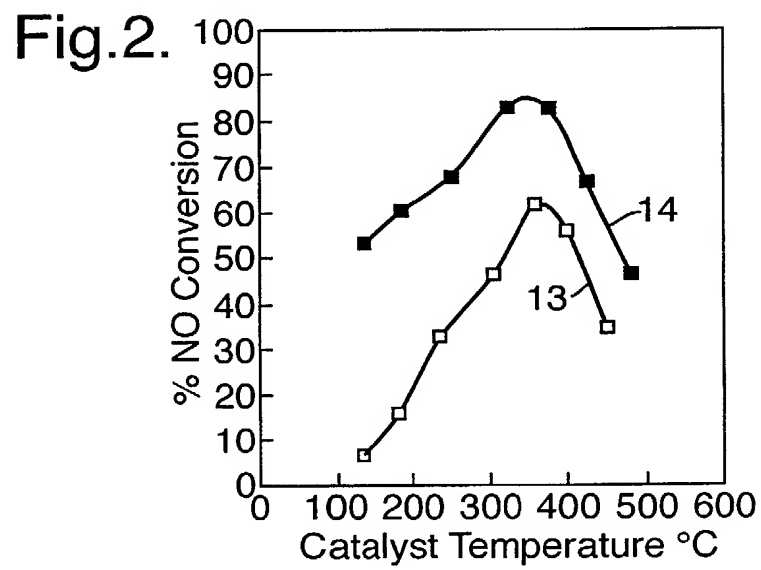
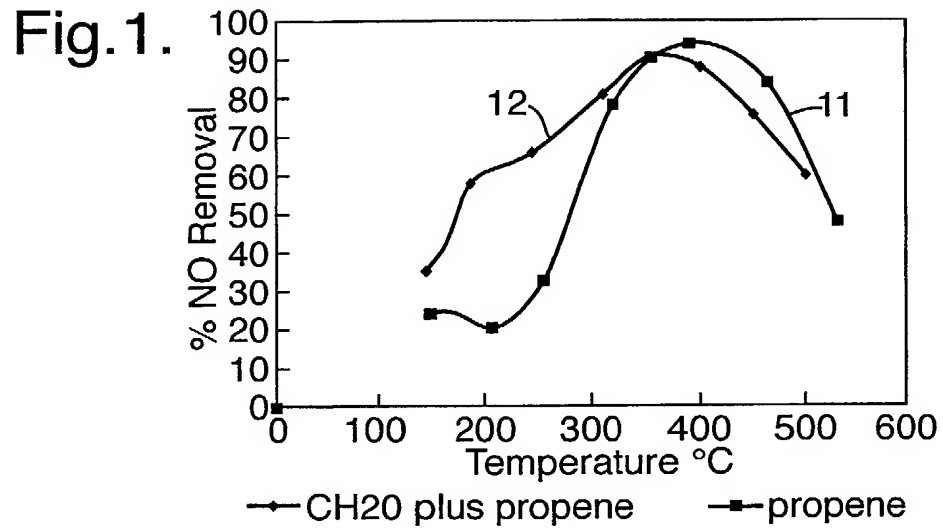


Fig.4.

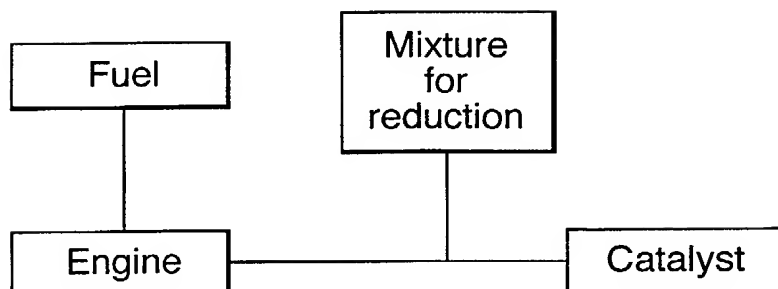


Fig.5.

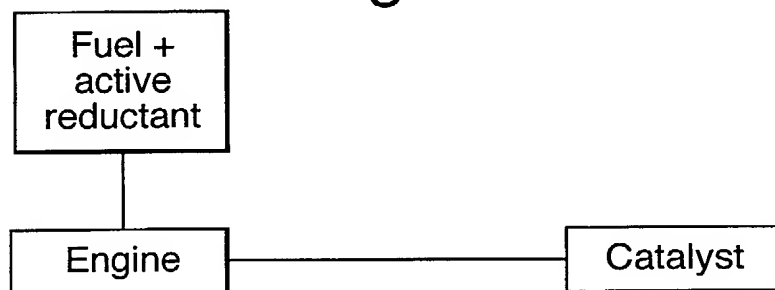


Fig.6.

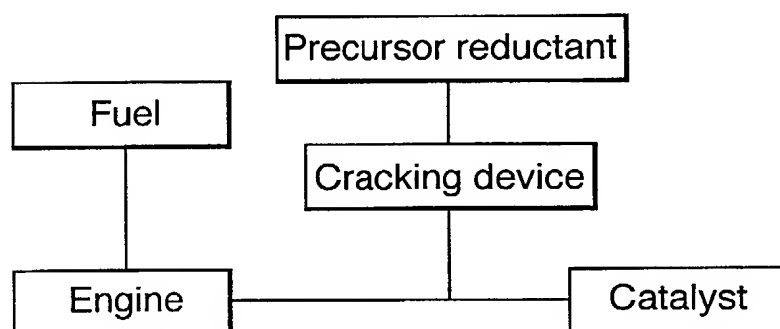


Fig.7.

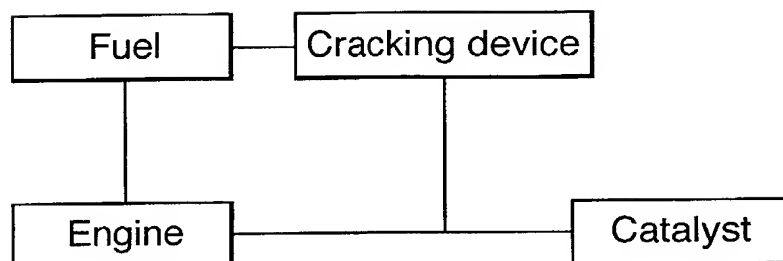


Fig.8.

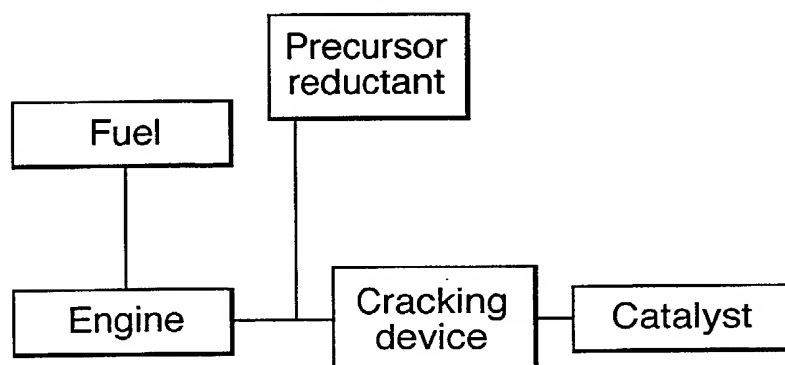
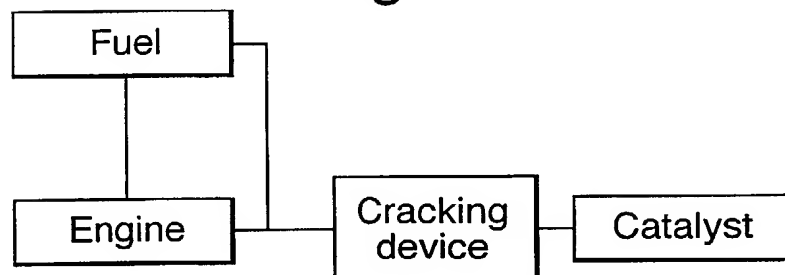


Fig.9.



Removal of Nitrogen Oxides from Effluent Gases

The present invention relates to the removal of nitrogen oxides from gaseous effluent and more particularly to the treatment of the exhaust gases from internal combustion engines to reduce the emissions of nitrogen oxides.

One of the major problems associated with the development and use of internal combustion engines is the noxious exhaust emissions from such engines. Two of the most deleterious materials, particularly in the case of diesel engines, are particulate matter (primarily carbon) and oxides of nitrogen such as nitric oxide (NO) and nitrogen dioxide (NO₂) often referred to as (NO_x).

Excessive levels of NO_x are also produced by spark-ignition engines operating in what is known as 'lean burn' mode in which the air: fuel ratio is higher than that required for stoichiometric combustion. It is also appreciated that alternative fuels and hybrid type combustion engines, as an example which may burn diesel fuel and/or natural gas, may also pose a similar problem. Increasingly severe emissions control regulations are forcing internal combustion engine and vehicle manufacturers to find more efficient ways of removing these materials in particular from internal combustion engine exhaust emissions.

One of the ways in which emissions are being reduced is by modifying the combustion process in the engine. Modifications include altering injection timing, engine design, common rail systems and exhaust gas recirculation (EGR) but all have certain limits for practical engine operation. Unfortunately, in practice, it is found that combustion techniques which improve the situation in

relation to one of the above components of internal combustion engine exhaust emissions tend to worsen the situation in relation to the other.

5 There are however numerous aftertreatment techniques
being developed to remove NO_x emissions from exhaust
gases from internal combustion engine exhaust as well as
other waste gas sources. In general, practical NO_x
reduction systems for internal combustion engines are
10 reliant on passing the exhaust gases across a catalyst.
There are generally two types of catalytic reduction
methods used, non-selective and selective catalytic
reduction (SCR). This invention is concerned primarily
with SCR systems and requires a suitable reductant or
15 reducing agent to be present or added to the exhaust gas.
Typical reductants for this purpose are urea or ammonia,
but these are not the most practical for mobile vehicle
applications. This is because this needs additional space
for the reductant tank on the vehicle and a supply
20 infrastructure to allow the reductant to be replenished.
SCR catalysts can however perform very effectively using
hydrocarbons, normally found in the combustion engine
exhaust, as the reductant for a certain range of
temperatures. One of the key issues with this approach is
25 whether the exhaust gas has the required concentration of
hydrocarbon reductant present to promote the required
selective catalytic reactions to reduce NO_x to nitrogen.
The concentration of hydrocarbons may be altered, if
there is insufficient in the exhaust, by for example,
30 adding a post-injection of fuel into the combustion
chamber or by injecting fuel into the exhaust. One
recently developed method is to use non-thermal plasma to
activate the hydrocarbon, which may be in the form of

additional fuel, to promote the catalytic NO_x reduction to nitrogen as disclosed in WO99/12638.

5 Considerable effort has been dedicated to the development of catalysts for the reduction of NO_x from diesel exhausts. The paper 'Selective Catalytic Reduction of NO_x with N-Free Reductants' by M. Shelef published in Chem. Rev. 1995 pages 209-225 is a comprehensive review in particular of the use of zeolites for the reduction of
10 the NO_x content of internal combustion engine exhaust gases. Other catalysts are mentioned but not dealt with comprehensively. The more recent review by Parvaiescu et al., 'Catalytic Removal of NO' published in Catalysis Today, volume 46 (1998) pp 233 - 316 is a comprehensive
15 document on the range of materials that have been evaluated for the selective catalytic reduction of NO_x. This is catalysis such as zeolites, including metal-exchanged zeolites, oxides such as simple oxides, for example Al₂O₃, V₂O₅, complex oxides such as perovskites
20 and precious metal supported oxides, in the presence of reducing agents such as hydrocarbons or ammonia. All of the materials described in this review are used solely as thermally active catalysts.

25 Multi-stage systems for the SCR of NO_x have also been developed. These systems have concentrated upon modification of the NO/NO₂ balance to cause the bulk of the NO_x in the exhaust to be converted to be in the form of NO₂ in the first stage, and reducing the resulting NO_x
30 (now mainly NO₂) using a selective catalytic reduction process over a suitable catalyst.

Iwamoto et al in the article 'Oxidation of NO to NO₂ on a Pt-MFI Zeolite and Subsequent Reduction of NO_x by C₂H₄ on an In-MFI zeolite: a novel de-NO_x strategy in excess oxygen' published in Chemical Communications pages 5 37-38, 1997, describes the use of a two-stage whereby NO is first oxidised to NO₂ by a Pt containing MFI zeolite oxidation catalyst with maximum conversion at 423 K. Hydrocarbon, C₂H₄, is added to the oxidised gas stream that is passed over an In-containing MFI zeolite 10 catalyst, whereupon the selective catalytic reduction of NO₂ to N₂ takes place in the presence of oxygen.

PCT application WO98/09699 discloses an arrangement in which oxygen-rich exhaust gases are passed through a 15 bed of an oxidising catalyst such as platinum-doped alumina in which NO_x in the exhaust gases is oxidised to NO₂. Hydrocarbons are mixed with the effluent from the oxidiser and the mixture is passed through a bed of reducing catalyst, γ-alumina in which the NO₂ and 20 hydrocarbons are reduced / oxidised in turn to give N₂, CO₂ and H₂O.

Multi-stage systems using a combination of a non-thermal plasma and a catalyst for the treatment of NO_x 25 components of diesel exhaust have also been proposed.

GB Patent Application 2,270,013 A describes a two-stage system in which exhaust emissions from internal combustion engines are subject to a low temperature 30 plasma and then passed over a catalyst that is downstream of the plasma. Although not specifically mentioned in GB

Patent Application 2,270,013 A, it will be appreciated that the exhaust emissions can contain nitrogen oxides.

US patent 5,711,147 describes a two-stage in which a
5 non-thermal plasma oxidises NO in the gas stream to NO₂
and the latter then undergoes selective catalytic
reduction to N₂ in the presence of C₃H₆ over γ -Al₂O₃
catalyst. The system is for use with oxygen-rich exhaust
gases from diesel and lean-burn spark ignition engines.
10 In the system described a hydrocarbon such as diesel fuel
is cracked into simpler hydrocarbons by a corona
discharge and then is mixed with the oxygen-rich exhaust
gases from which NO_x is to be removed. The mixed
hydrocarbons and exhaust gases are then passed through
15 another region of corona discharge. In this region NO_x is
oxidised to NO₂. The NO₂ plus excess hydrocarbons are
passed through a bed of catalyst, which acts to reduce
the NO₂ to N₂ and to oxidise the hydrocarbons to CO₂ and
H₂O. No plasma is involved in the reduction stage.
20 Cracking of the fuel by corona discharge is intended to
maximise the proportion of smaller hydrocarbon species in
the reductant, the process is not described as providing
a mixture of reductant and activated hydrocarbon species
in carefully controlled proportion to promote the
25 activity of the NO₂ reduction catalyst. There is a
requirement for the pre-conversion of NO to NO₂ before
selective catalytic reduction in US 5,177,147 as the
catalyst used is more efficient for the reduction of NO₂
than for the reduction of NO.

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WO00/18494 describes a method and apparatus in which
a gas stream containing NO and hydrocarbon is passed

through a plasma and then over a catalyst comprising a microporous material, particularly a zeolite, resulting in the reduction of NO_x to nitrogen. Results shown in WO00/18494 indicate that the percentage NO_x reduction was
5 as high as 77%, but it could be as low as 4% depending on the catalyst used for temperatures in the range 373-573 K.

GB patent 2,274,412 discloses a method and apparatus
10 for removing particulates and other pollutants from internal combustion engine exhaust gases. In addition to removing particulates by electric discharge assisted oxidation such as by use of a non-thermal plasma, there is disclosed the reduction of NO_x gases to nitrogen, by
15 the use of a bed of pellets adapted to catalyse the NO_x reduction.

PCT specification WO99/12638 describes a method for treatment of internal combustion exhaust gases in which
20 nitrogen oxides are removed by a process which includes the operations of passing hydrocarbons through a plasma in which there is a first material having oxidative properties in the presence of a plasma thereby producing reactive activated hydrocarbons and contacting a mixture
25 of the activated hydrocarbons and the exhaust gases with a second material adapted in the presence of hydrocarbons to catalyse the reduction of nitrogen oxides to nitrogen.

PCT specification WO00/29727 concentrates upon the
30 method of making activated hydrocarbons and does not disclose an optimum composition of hydrocarbons for promoting NO_x reduction on a catalyst adapted for the purpose. It is disclosed that small and or oxygenated hydrocarbon species which may or may not include

formaldehyde and acetaldehyde are the preferred products of the cracking process and that optimisation of the system would be by maximising the fraction of these species in the hydrocarbon passed over the NO_x reduction catalyst. However an optimum composition of a hydrocarbon reductant mixture is not referred to, nor is the specific role of certain concentrations of activated species.

It is known that the nature of the hydrocarbon used as a reductant for the selective catalytic reduction of NO_x can influence the selective catalytic reduction of NO_x by a catalyst.

Eranen et al in their paper SAE 2000-01-2813 report that different reductants such as a propene, propane, octane, iso-octane, 1-octene, octanal, octanol, octanoic acid and diesel fuel result in different levels of NO_x reduction to N₂ by Ag doped alumina catalyst.

Shimizu et al reported, in their paper 'Catalytic performance of Ag-Al₂O₃ catalyst for the selective catalytic reduction of NO by higher hydrocarbons' published in Applied Catalysis B Environmental 25 (2000) 239-247, that the rate of NO conversion to N₂ increased as the carbon number of the reductant used was increased from one to eight (methane to octane) at the same time, the temperature at which the peak reduction of NO to N₂ occurred was reduced from 800 K to 600 K.

Silver-based catalysts have been described for the reduction of NO_x in vehicle emissions. In the papers by Miyadera "Alumina-supported silver catalysts for the selective reduction of nitric oxide with propene and

oxygen-containing organic compounds" published in Applied Catalysis B: Environmental, volume 2, (1993) pages 199-205, and Miyadera and Yoshida "Alumina-supported silver catalysts for the selective reduction of nitric oxide with propene" published in Chemistry Letters, (1993), page 1483 a 2% Ag-alumina catalyst showed promising hydrothermal stability for NO_x reduction. Added propene and partially oxygenated hydrocarbons, such as 2-propanol, were effective reductants. Masuda et al in the article "Silver promoted catalyst for removal of nitrogen oxides from emissions of diesel engines" in Applied Catalysis B: Environmental, volume 8, (1996), pages 33-40 showed that 3% Ag-mordenite was a promising lean NO_x catalyst compared to Ag-ZSM-5 and Ag-alumina with acetone (CH₃COCH₃) as reductant. Bethke and Kung in the paper "Supported Ag catalysts for the lean reduction of NO with C₃H₆" published in Journal of Catalysis, volume 172, (1997), page 93 showed that the oxidation state of silver affects its catalytic activity for the reduction of NO_x. Another silver containing compound, silver aluminate, AgAl₂O₄, doped with 0.1 weight % WO₃ was shown to be a promising catalyst for the reduction of NO_x by Nakatsuji et al in the paper "Catalytic reduction system of NO_x in exhaust gases from diesel engines with secondary fuel injection" published in Applied Catalysis B: Environmental, volume 17, (1998), pages 333-345. Keshavaraja et al in an article 'Selective catalytic reduction of NO with methane over Ag-alumina catalysts' published in Applied Catalysis B:Environmental, volume 27, pages L1-L9, 2000 used CH₄ for the selective reduction of NO over silver-alumina catalysts at temperatures between 723-923 K with Ag loading of 1-7 weight percent.

Meunier et al have discussed the role of silver-alumina catalysts on the selective catalytic reduction of NO by propene in an article 'Mechanistic aspects of the selective reduction of NO by propene over γ -alumina and silver-alumina catalysts' published in Journal of Catalysis, volume 187, pages 493-505, 1999. High silver loading, 10 percent by weight produced N_2O while a low loading, 1.2 percent by weight, was effective for the selective catalytic reduction of NO to N_2 . Adsorbed organo-nitrogen compounds such as organo-nitrites were intermediate species in the reaction.

Masters and Chadwick showed that oxygenated hydrocarbons, methanol and dimethyl ether can reduce NO to N_2 under lean conditions by selective catalytic reduction over γ -alumina. This work, 'Selective reduction of nitric oxide by methanol and dimethyl ether over promoted alumina catalysts in excess oxygen', published in Applied Catalysis B: Environmental, volume 23, pages 235-246, 1999 showed that molybdena (MoO_3) additions improved the catalytic activity at temperatures lower than those required in the case of $\gamma-Al_2O_3$ alone. Surface formyl species were an intermediate product in the reaction.

25

None of the aforementioned prior art however describes the metering of a predetermined mixture of hydrocarbons preferably including formaldehyde to act as an enhanced reductant composition to improve reduction of NO_x to N_2 over a silver alumina catalyst. The use of silver alumina is believed to be especially important for NO_x reduction as it displays significant selectivity towards NO reduction to N_2 . This reduces the requirement

30

of many other catalytic approaches for pre-converting NO to NO₂ before reducing NO₂ to N₂.

An object of the present invention is to improve the SCR
5 of NO_x over a silver alumina catalyst by using a controlled mixture of hydrocarbon reductant, which preferably includes formaldehyde. More specifically it is an object of the invention to improve in this way the reduction activity of the silver alumina catalyst,
10 reducing NO_x to N₂, over the typical temperature range of vehicle exhausts, and especially to effect improvement at lower temperatures.

According to the invention there is provided a
15 method for use in the treatment of gaseous effluent containing oxides of nitrogen(NO_x) by reduction over a silver alumina catalyst of NO_x to N₂, which method comprises introducing into the gaseous effluent a reductant mixture of controlled constitution and
20 including hydrocarbon as at least one constituent of the mixture. Where the effluent gases are exhaust gases from a combustion process, such as from an internal combustion engine, the hydrocarbon reductant mixture may be produced by adding at least one additional selected hydrocarbon to
25 the hydrocarbons already present in the exhaust gases as a the result of the combustion process, or by creating the mixture from these constituents of the exhaust gases. The hydrocarbon reductant mixture may for example include the engine out hydrocarbons and a partially oxidised
30 hydrocarbon. Preferably the partially oxidised hydrocarbon is formaldehyde. However, other oxygenated hydrocarbons such as acetaldehyde may be suitable. The reductant mixture may include other species that are not hydrocarbons, but which act when present in controlled

proportions to improve the reduction performance over a silver alumina catalyst.

The amount of added hydrocarbon or other species
5 introduced to improve the catalytic reduction of NO_x to N_2
over silver alumina is kept to a minimum. The
concentration of the reductant mixture, including added
constituent such as formaldehyde or constituent created
in the combustion exhaust gases, is conveniently
10 specified by the ratio of carbon atoms to NO_x molecules
(C_1 : NO_x ratio). Preferably in accordance with this
invention the reductant mixture has a C_1 : NO_x ratio of
10:1 or less. Preferably this ratio is 6:1 or less. More
preferably this ratio is as low as 3:1 or less. The
15 composition and concentration of reductant mixture
required is dependent upon the catalyst, the
concentration of NO_x in the exhaust gas and the
temperature of the exhaust gas.

20 Specific methods embodying the invention will now be
described by way of example and with reference to the
drawings filed herewith, in which:

Figure 1 is a graph showing the effect of adding
25 formaldehyde to propene in a simulated internal
combustion engine exhaust passed over a silver alumina
catalyst,

Figure 2 is a graph showing the effect of adding
30 formaldehyde to RF 73 diesel fuel in an internal
combustion engine exhaust passed over a silver alumina
catalyst,

Figure 3 is a graph showing a comparison of the effect of a reductant mixture of formaldehyde and propene in a simulated internal combustion engine exhaust passed over a silver alumina catalyst when the formaldehyde has been produced in or activated by a plasma as compared with formaldehyde introduced from a non-plasma source, and

Figures 4 to 9 are block diagrams illustrating a variety of configurations for introducing the reductant mixture into an internal combustion engine exhaust system.

Figure 1 shows the results of an experiment in which a simulated synthetic exhaust of 10% O₂, 540ppm NO, Propene (C₃H₆) to make a C₁: NO_x ratio of 6, N₂ balance, was passed over a 2% silver doped alumina catalyst whose temperature was controlled across a range of typically ~100°C to 550°C. The propene is used to simulate engine out hydrocarbon emissions which are produced as a result of the combustion process. As curve 11 in Figure 1 illustrates, the percentage NO conversion to N₂ with the silver alumina catalyst in the presence of the propene reductant alone increases from 25% at temperatures greater than ~250°C. Maximum conversion of 90% occurs at ~400°C above which point the conversion falls to 50% at 550°C.

The exhaust gas composition was then modified such that the hydrocarbon reductant mixture contained propene and ~40ppm formaldehyde such that the C₁: NO_x ratio of 6 was maintained. This simulated exhaust gas was passed across the silver alumina catalyst and the temperature controlled across the range as before. The general NO_x

conversion profile is similar to the previous case where the reductant was only propene. However, as can be seen in curve 12 in Figure 1, the reductant mixture of propene and formaldehyde has improved the performance of the catalyst especially at the lower temperatures. For example, at 200°C the percentage NO conversion to N₂ with the silver alumina catalyst in the presence of the reductant mixture has increased from 25% to 60%. Maximum conversion of 90% occurs at ~350°C, above which point the conversion falls. A further advantage is provided in that the overall activity window of the catalyst for NO conversion to N₂ has also been increased.

These beneficial effects have also been observed when a reductant mixture of formaldehyde and diesel fuel, rather than propene to represent the engine out hydrocarbon, has been used. This is illustrated in Figure 2 in which curve 13 shows the percentage NO conversion to N₂ over the silver alumina catalyst in the presence of RF73 diesel fuel alone and curve 14 shows the improvement when ~40ppm formaldehyde is mixed with the diesel fuel.

Promotion of NO_x reduction using a reductant mixture of hydrocarbon species of controlled constitution appears to be independent of the method by which the mixture is prepared or introduced into the exhaust. This is illustrated in Figure 3, which shows that there is little difference in NO_x reduction performance as between a mixture created by blending raw components (curve 15 in Figure 3) and a substantially equivalent mixture (curve 16 in Figure 3) created by controlled treatment of a mixture of propene and engine exhaust gases with a non-thermal plasma.

Evidence from thermal studies indicates that a reductant mixture of the desired constitution can form as catalytic NO_x reduction proceeds at elevated temperature in exhaust gases containing unburnt hydrocarbons (explaining the high temperature performance illustrated by curve 11 in Figure 1). By providing the desired constitution of reductant mixture at lower temperature, effective NO_x reduction is achieved at lower exhaust gas temperatures.

10

The optimum composition of the reductant mixture will be dependent upon the catalyst, the exhaust gas composition, especially the hydrocarbons and the NO_x , and temperature. For the examples provided herein, increasing the formaldehyde concentration up to 60 ppm in the reductant mixture improved the effect but higher concentrations showed no appreciable benefit. It is important to note that formaldehyde alone does not appear to give this beneficial effect with the silver alumina catalyst. Formaldehyde at various concentrations, typically 10-100 ppm, was passed over the catalyst in an exhaust stream of 10% O_2 , 540 ppm NO balance N_2 . There was an absence of any significant NO removal with this exhaust stream across the range of exhaust temperatures, typically 100°C to 550°C. This indicated that formaldehyde alone does not provide substantial benefit for NO reduction across a silver alumina catalyst.

30

Another important observed effect is that addition of formaldehyde to the reductant mixture may reduce the sensitivity of the catalyst to the nature of the reductant. The NO_x reduction activity profile of silver alumina when the hydrocarbon reductant is propene alone

is subtly different compared with the activity profile when the reductant is diesel fuel alone. When a mixture of propene or fuel reductant and formaldehyde is used the respective activity profiles become much more similar. It
5 appears that relatively small concentrations of formaldehyde can activate SCR of NO_x over the silver alumina catalyst.

These beneficial effects of the addition of small
10 quantities of formaldehyde may well be achieved with catalysts other than silver alumina for NO_x reduction. Examples of other catalysts, the reduction activity of which may benefit in this way include, but are not limited to, zeolites, including doped zeolites such as
15 Ag, Na, In, Cu, aluminas including activated aluminas which may be doped or coated. The invention is also conveniently applicable to mixed catalyst beds and coatings.

20 The required reductant mixture may be produced in a number of ways.

The reductant mixture can be made by metering a hydrocarbon such as formaldehyde from a separate storage
25 tank into the engine out exhaust gases that contain hydrocarbons and NO_x . The resultant mixture would then pass over the catalyst. This method may be used in combination with post injection of fuel into the cylinder or directly into the exhaust if there is insufficient
30 engine out hydrocarbons to promote catalytic NO_x reduction.

The reductant mixture such as propene and formaldehyde could also be pre-mixed and subsequently

metered directly into the exhaust gases from a storage tank. This is illustrated by Figure 4 and would be useful if the engine out exhaust did not contain sufficient hydrocarbons to achieve the desired $C_1: NO_x$ ratio for
5 reduction.

The reductant mixture or components of it may be created by processing a precursor using methods such as thermal or catalytic cracking, catalytic oxidation (or
10 reduction) or non-thermal plasma activation. This is illustrated by Figure 6. Figure 7 illustrates an alternative where the precursor is the diesel fuel itself. Figure 8 illustrates an arrangement where processing is applied to a mixture of the engine exhaust
15 itself and a precursor reductant. Figure 9 illustrates a similar arrangement where the processing is applied to the diesel fuel itself together with the engine exhaust to form the reductant mixture. It is possible that the reductant or precursor may be incorporated into the
20 combustion engine fuel. On combustion this additive would combine with the engine out hydrocarbons to provide the reductant mixture required for catalytic NO_x reduction. This is illustrated in Figure 5. It may well be possible to operate the engine in a manner, which provides the
25 reductant mixture required directly.

The metering and control of the reductant mixture will be dependent upon the composition of the exhaust gas and will be governed by the engine-operating map. For
30 example it may well be that as torque and speed settings change the exhaust composition and temperature will require more or less reductant mixture to be present. At some points especially at the higher exhaust gas temperatures it may not be necessary to mix any
35 reductants i.e. no requirement for formaldehyde, because

the engine out hydrocarbons alone are sufficient at the higher temperature to promote the catalytic NO_x reduction.

5 The invention is not restricted to the details of the foregoing examples. For instance the silver alumina catalyst used in the examples had not been specifically hydrothermally aged. It will be appreciated that hydrothermally aged silver alumina may be used for
10 selective catalytic reduction of NO_x, possibly with advantage.

Claims

1. A method for use in the treatment of gaseous effluent containing oxides of nitrogen (NO_x) by reduction over a silver alumina catalyst of NO_x to N_2 , which method comprises introducing into the gaseous effluent a reductant mixture of controlled constitution and including hydrocarbon as at least one constituent of the mixture.
2. A method as claimed in claim 1 for use in the treatment of exhaust gases from a combustion process, such as from an internal combustion engine, wherein the hydrocarbon reductant mixture is produced by adding at least one additional selected hydrocarbon to the hydrocarbon or hydrocarbons already present in the exhaust gases as a result of the combustion process.
3. A method as claimed in claim 1 for use in the treatment of exhaust gases from a combustion process, such as from an internal combustion engine, wherein the hydrocarbon reductant mixture is produced by creating the mixture from the constituents of the exhaust gases.
4. A method as claimed in claim 1 or claim 2, wherein the hydrocarbon reductant mixture comprises hydrocarbon or hydrocarbons already present in the exhaust gases and a partially oxidised hydrocarbon.
5. A method as claimed in claim 4, wherein the partially oxidised hydrocarbon is formaldehyde.
6. A method as claimed in claim 4, wherein the partially oxidised hydrocarbon is acetaldehyde.

7. A method as claimed in any of the preceding claims,
wherein the reductant mixture includes other species that
are not hydrocarbons, but which act when present in
controlled proportions to improve the reduction
5 performance over a silver alumina catalyst.

8. A method as claimed in any of the preceding claims,
wherein the reductant mixture has a C_1 : NO_x ratio of 10:1
or less.
10

9. A method as claimed in claim 8, wherein the
reductant mixture has a C_1 : NO_x of 6:1 or less.

10. A method as claimed in claim 8 or claim 9, wherein
15 the reductant mixture has a C_1 : NO_x ratio of 3:1 or less.

11. A method substantially as hereinbefore described in
any of the examples.

20 12. A method substantially as hereinbefore described in
any of the examples with reference to Figures 4 to 9 of
the drawings.

25 15526 LgCm

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INVESTOR IN PEOPLE

Application No: GB 0109734.4
 Claims searched: 1-12

Examiner: Dr Albert Mthupha
 Date of search: 31 July 2001

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
 UK CI (Ed.S): B1E; B1W (WAX, WD, WX)
 Int CI (Ed.7):
 Other: ONLINE : EPODOC, JAPIO, WPI.

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0788829 A1 SAKAI, see page 2 lines 44-55, page 5 lines 36-49, Claims 1, 6.	1, 2, 5, 6 at least.
X	EP 0682975 A1 RIKEN, see Claims 1, 14.	1, 2, 5, 6 at least.
X	EP 0577438 A2 RIKEN, see page 3 lines 55-57, page 7 line 39, page 9 line 35-page 10 line 26, Claims 1, 2, 3, 8.	1, 2, 5, 6 at least.
X	WPI Abstract AN 2000-621293 [60] & JP 2000213334 A (TOKYO GAS), note Abstract.	1, 2 at least.
X	WPI Abstract AN 1998-550096 [47] & JP 10244155 A (SAKAI), note Abstract.	1, 2, 5, 6 at least.
X	WPI Abstract AN 1995-260189 [45] & JP 7163878 A (RIKEN), note Abstract.	1, 2, 5, 6 at least.
X	WPI Abstract AN 1995-370618 [48] & JP 7251072 A (SUMITOMO), note Abstract.	1, 2, 5, 6 at least.

X Document indicating lack of novelty or inventive step
 Y Document indicating lack of inventive step if combined with one or more other documents of same category.
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 P Document published on or after the declared priority date but before the filing date of this invention.
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